Effect of Residual Solvent on Exposure Sensitivity under EUV and Low-Energy Electron Irradiation in PHS-Boc Resists

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Outline

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1. Background and Objectives
2. Sample Preparation
3. Thin-Film Characterization
    - Residual Solvent by Thermal Desorption GC-MS
    - Chemical Composition Distribution by RSoXS
    - Film Density by XRR
4. Sensitivity Evaluation
    - EUV Exposure
    - LEEFET
5. Summary

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Background and Objectives

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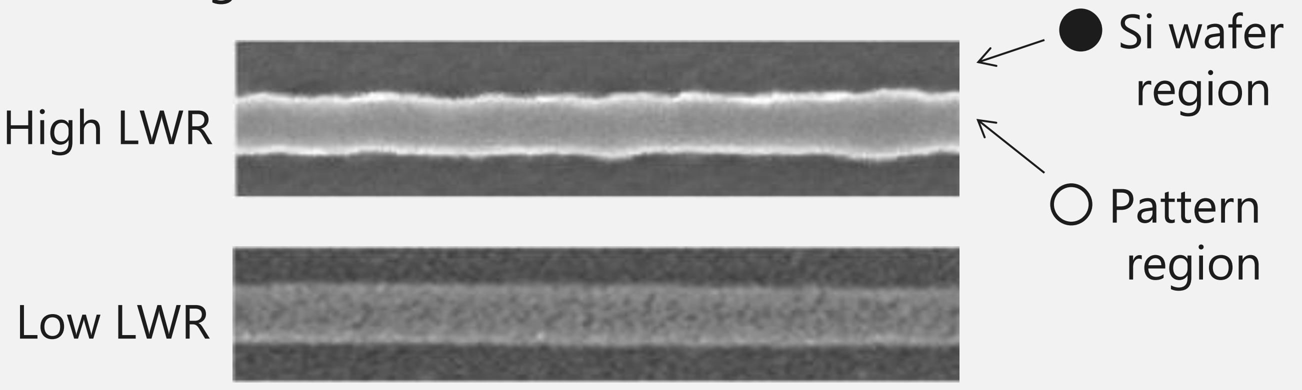
- ✓ Non-uniform chemical composition distributions in resist thin films can contribute to line-width roughness (LWR) in EUV lithography.
- ✓ We hypothesized that solvent polarity and residual solvent can affect thin-film homogeneity and provide a route to reducing LWR.
- ✓ In this study, we connect thin-film properties, such as chemical distribution and density, with EUV and low-energy-electron exposure sensitivity.

SEM Images of Resist L/S Patterns



Measurement Platform at NewSUBARU

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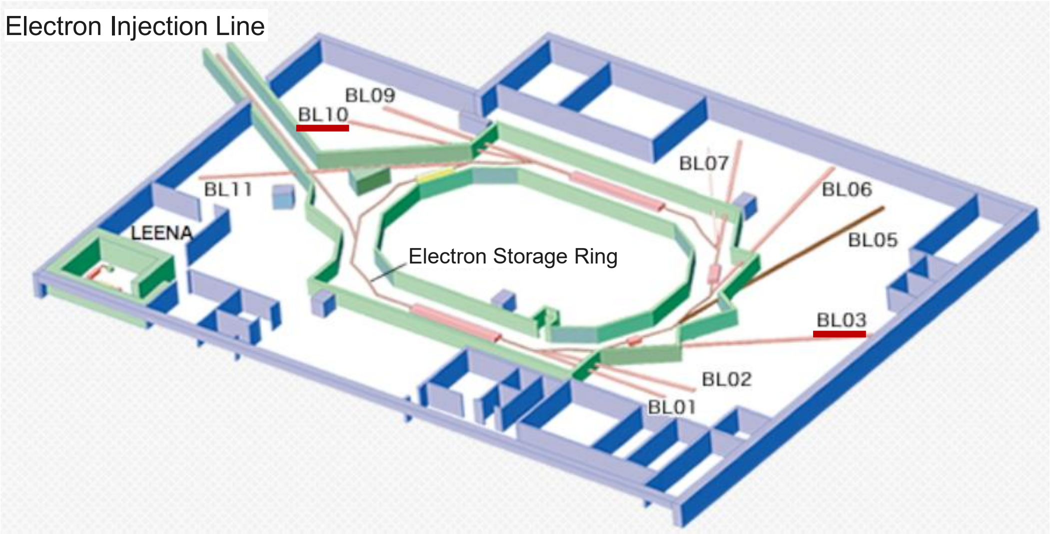
Schematic Illustration of the NewSUBARU facility



Source: University of Hyogo, NewSUBARU website

This study was conducted using instruments at the NewSUBARU synchrotron radiation facility.

Thin-Film Characterization

- ✓ BL-10 : RSoXS for evaluating chemical composition distribution
- ✓ XRR : Average film density measurement

Sensitivity Evaluation

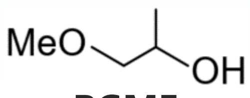
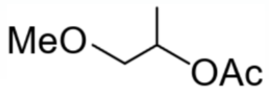
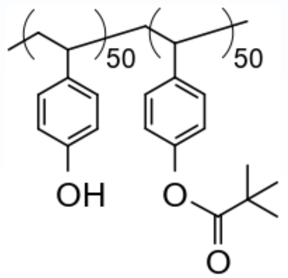
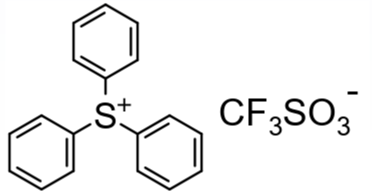
- ✓ BL-3 : EUV flood exposure
- ✓ LEEFET : low-energy electron flood exposure

This platform enabled us to relate thin-film properties to exposure sensitivity.

Outline

Sample Preparation

Materials List

Structure / Name	 **PGME**	 **PGMEA**	 **PHS-Boc** (Mw 19k)	 **TPST**
Boiling point (˚C)	120	146	-	-
Vapor pressure (kPa@20 ˚C)	1.2	0.5	-	-

✓This slide summarizes the materials used in this study.

✓PGME and PGMEA were selected as coating solvents. These two solvents have different boiling points and vapor pressures.

✓As the base polymer, we used PHS-Boc, a PHS-based polymer partially protected with Boc groups.

✓TPST was used as the photoacid generator (PAG).

Sample Preparation

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Preparation of 50-nm-Thick Resist Thin Films for Evaluation

Process	Preparation of Coating Solution →	Spin Coating →	Post-Apply Bake (PAB) →	Exposure / Post-Exposure Bake (PEB) →	Development / Rinse
Content	・x wt% PHS-Boc ・10 wt% TPST a) ・PGME or PGMEA	・Coated on Si wafers	・Solvent removal / Each bake temperature, 60 s	・EUV or low-energy electron exposure / 110 ˚C、90 s	2.38 wt% TMAH aq. / Ultrapure water
Evaluation	-	-	・GC-MS ・RSoXS ・XRR	・XRR	・Sensitivity evaluation - LEEFET - EUV

a) : Relative to PHS-Boc.

✓This slide summarizes the sample preparation process and the evaluation scheme.

✓The process flow proceeds from left to right.

✓We evaluated the samples from two viewpoints: thin-film characterization and exposure sensitivity.

- GC-MS, RSoXS, and XRR were used to characterize residual solvent, chemical heterogeneity, and average film density.
- LEEFET and EUV exposure were used to evaluate exposure sensitivity.

Outline

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Measurement of Residual Solvent by Thermal Desorption GC-MS

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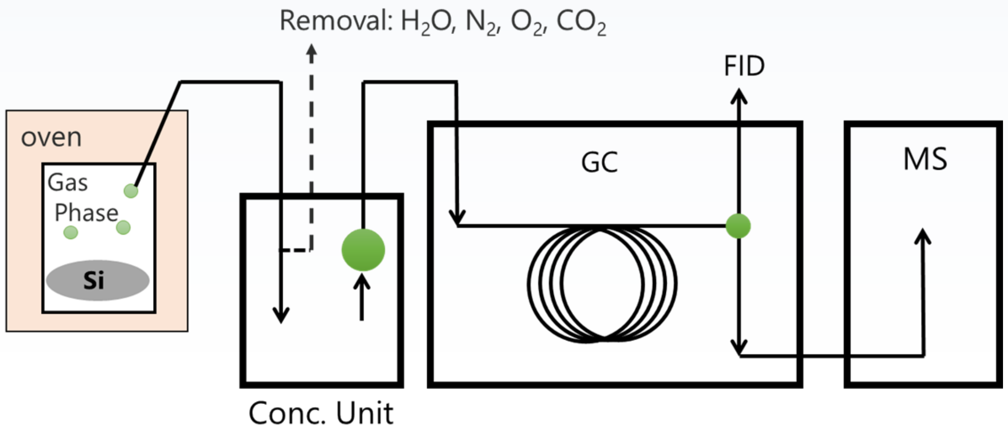


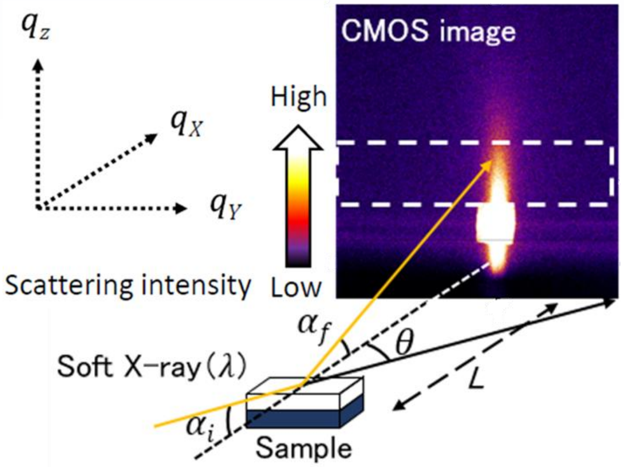
Solvent	Coating Concentration (wt%)	PAB Temperature (˚C)	Residual Solvent Content (ppb) [a)]
PGME	1.5	70	8
PGMEA	2.2	70	64
PGMEA	2.2	120	29

[a)] : Quantified using nitrogen standard gas containing 10 ppb toluene-*d8* as an internal standard.

- ✓ Thermal desorption GC-MS quantified solvent after PAB.
- ✓ At 70 ˚C PAB, PGMEA remained more than PGME, consistent with its lower volatility.
- ✓ For PGMEA, higher PAB temperature reduced the residual solvent content from 64 to 29 ppb.
- ✓ Residual solvent remains even in a 50-nm-thick resist film.

RSoXS Measurement System

- ✓ RSoXS detects nanoscale chemical heterogeneity through resonant soft-X-ray scattering.
- ✓ The measurement principle was introduced in presentation E2-5-4; here I focus on the energy conditions in this study.



Scattering vector

$$q_y = \frac{2\pi}{\lambda}(\sin\theta\cos\alpha_f)$$

Spatial frequency

$$d = \frac{\lambda}{2\sin\theta} = \frac{2\pi}{q_y}$$

λ : incident wavelength
θ : in-plane scattering angle
α_i : incident angle (5 °)
α_f : out-of-plane scattering angle
L : Camera length

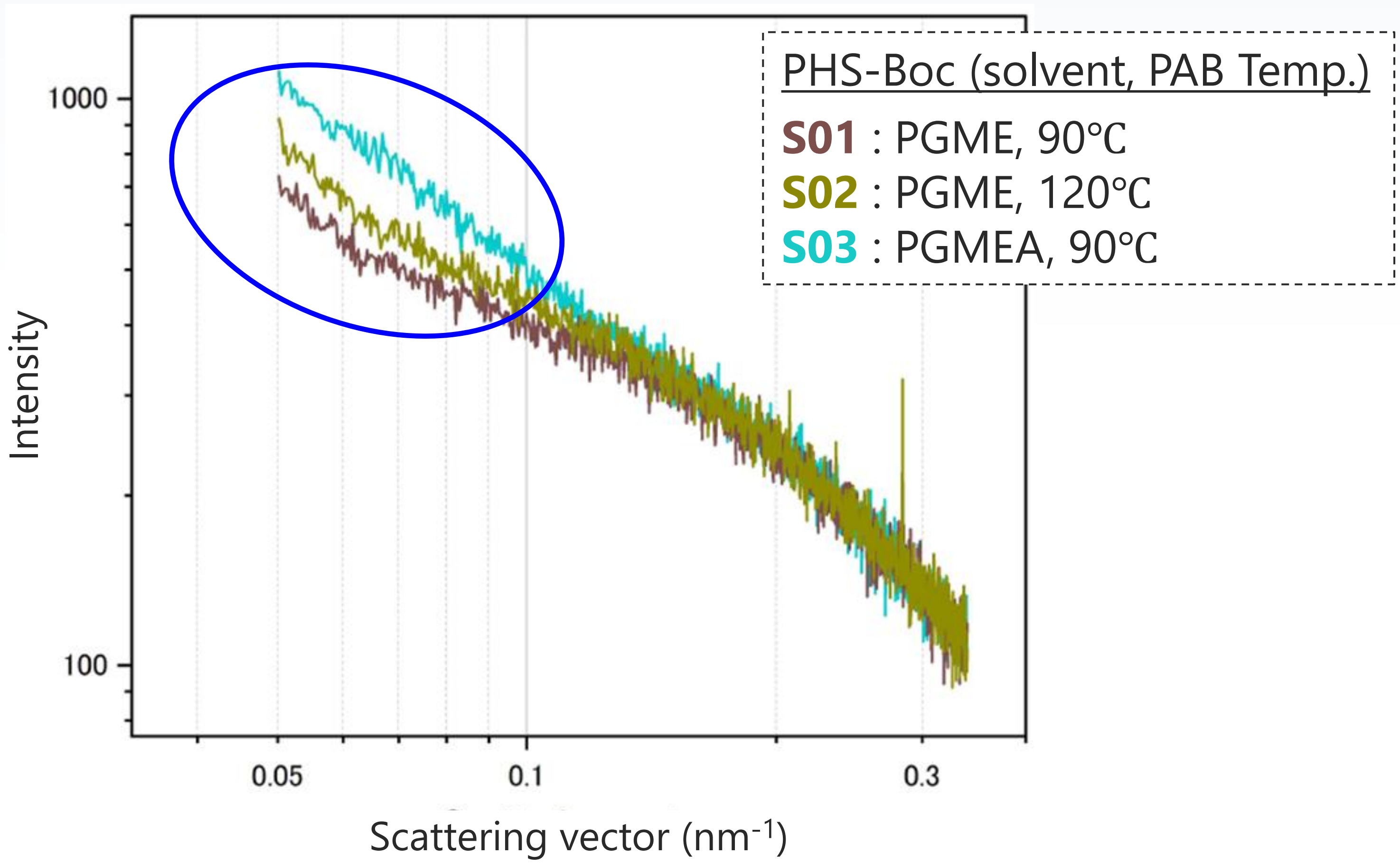
Incident energy

XAS was used to select the incident energy. Measurements were performed at 280 eV, where absorption at the C_K-edge is low and X-rays can penetrate into the film interior.

＜Absorption peak energy＞

286 eV：C=C (π^*)
289 eV：O-C=O (π^*)
296 eV：C-C (δ^*)
280 eV：Overall scattering independent of functional groups

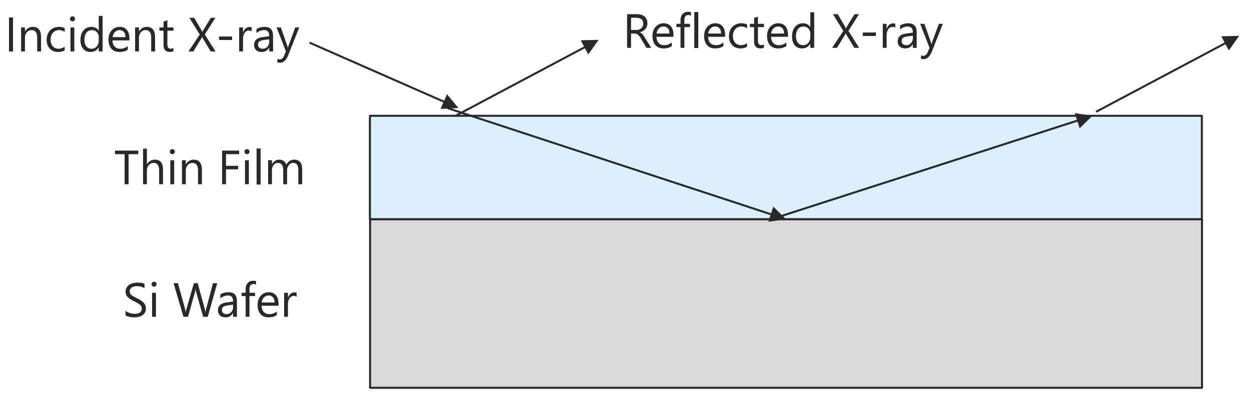
RSoXS Measurement Results

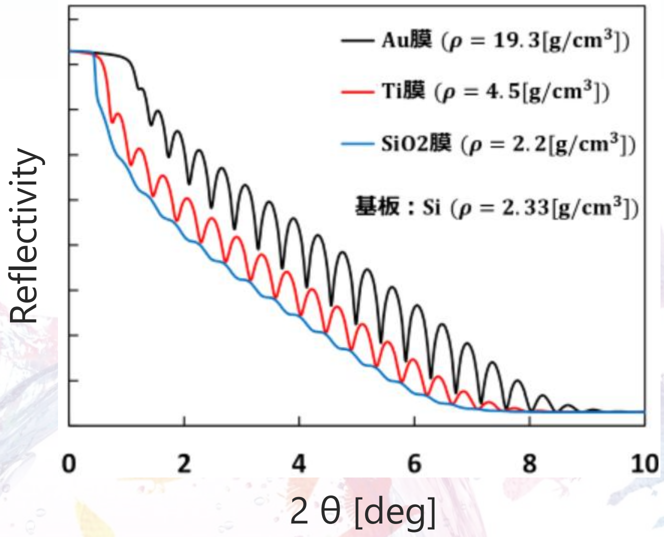


- ✓ At q = 0.05–0.1 nm^{-1}, steeper profiles were observed for the higher-PAB sample and for PGMEA compared with PGME.
- ✓ This suggests increased chemical composition heterogeneity or aggregation in the resist thin film.

About XRR Measurement

- ✓ X-ray reflectivity (XRR) provides film thickness, average film density, and surface/interface roughness from low-angle X-ray reflection profiles.





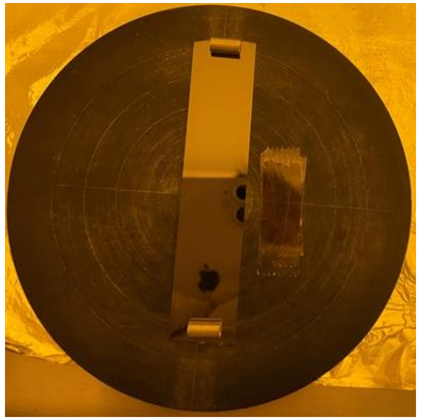
Source: Shimadzu Techno-Research, Inc. website

We used XRR to examine whether the RSoXS and sensitivity differences correlate with average film density.

XRR Measurement Results

Sample preparation for XRR measurements

Process	After PAB	Vacuum treatment in LEEFET	After PEB
Content	The resist-coated Si wafer was cut into 1-cm-wide pieces and mounted on the holder for XRR measurement.	The sample was placed in LEEFET and kept under vacuum for 30 min before XRR measurement.	After vacuum treatment, the sample was subjected to PEB and then measured by XRR.
Density (g/cm^3)	70 ˚C : 1.22	1.21	1.29
	90 ˚C : 1.26	-	-
	120˚C : 1.21	-	-
	130 ˚C : 1.24	1.26	1.24



- ✓ The average film density did not increase monotonically with PAB temperature.
- ✓ Density changes after LEEFET vacuum treatment and PEB depended on the initial PAB condition.
- ✓ Therefore, the exposure response cannot be fully explained by average film density alone.

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EUV Exposure Results

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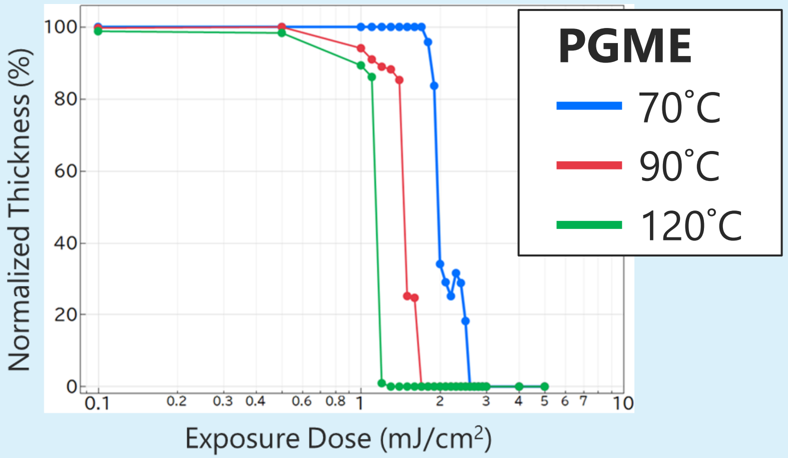
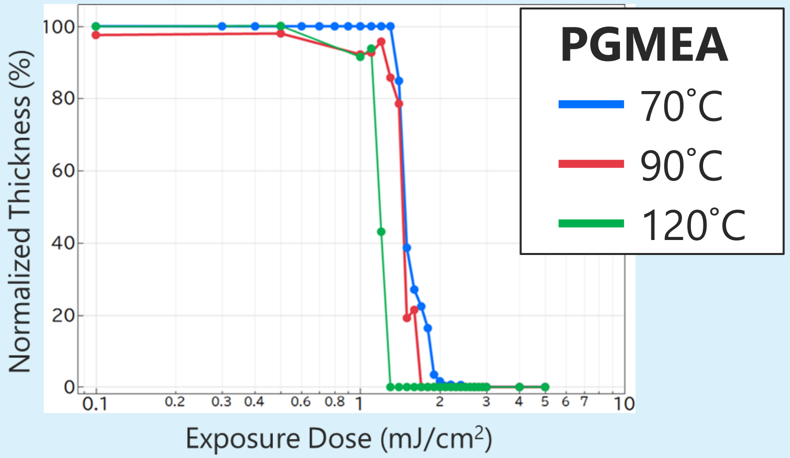
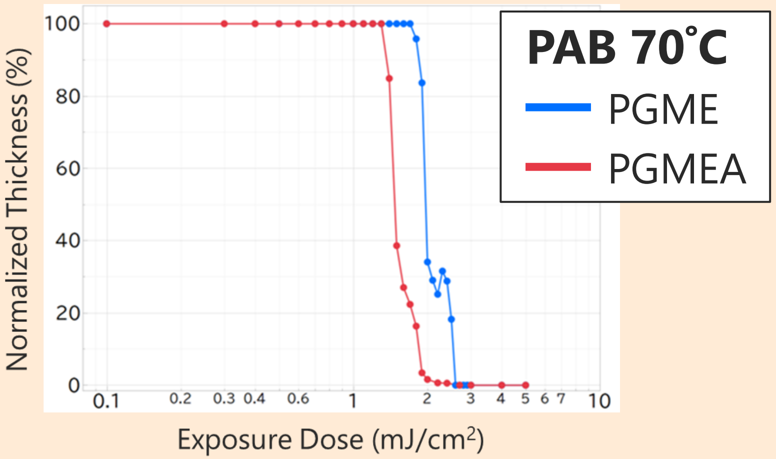
- Sensitivity curves were prepared after EUV exposure and development.
- The vertical axis shows the film-thickness loss ratio: $[(T_0 - T) / T_0] \times 100$.
- Here, T_0 is the unexposed film thickness and T is the exposed film thickness.

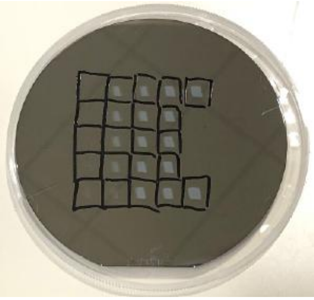
Effect of residual solvent





Effect of solvent species





Si wafer images after exposure and development

- ✓ For both PGME and PGMEA, sensitivity improved as the PAB temperature increased.
- ✓ PGMEA showed higher sensitivity than PGME.

LEEFET Experimental Method

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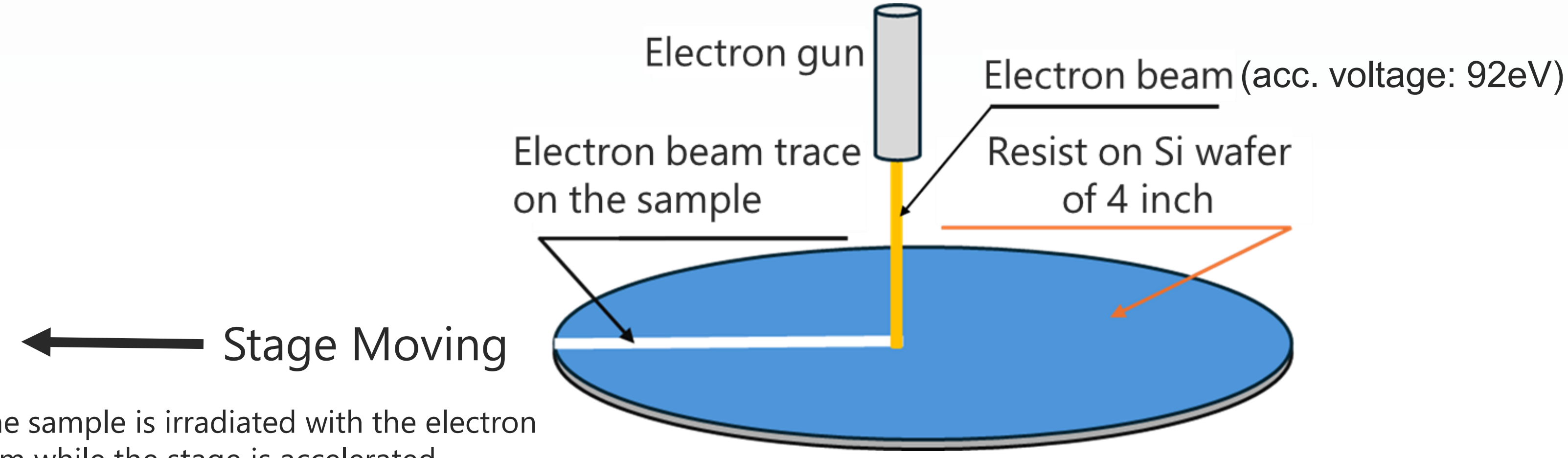
- LEEFET is an electron irradiation system independent of the NewSUBARU beamlines.
- It enables evaluation of low-energy-electron-induced effects related to EUV exposure.



* The sample is irradiated with the electron beam while the stage is accelerated.

- Dose (C/cm²) = beam current density (A/cm²) × exposure time (s)
- Beam diameter = Φ0.6 mm at 92 eV
- The beam current density can be set arbitrarily and remains constant during exposure.
- The actual dose depends on the stage speed.

Further details of LEEFET will be presented by our collaborator, Mr. Yamasaki, in the following presentation (E2-6-3).

LEEFET Measurement Results

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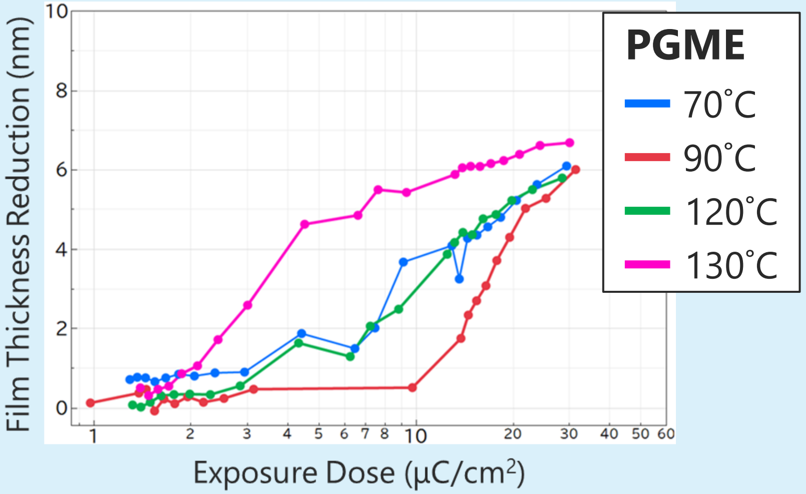
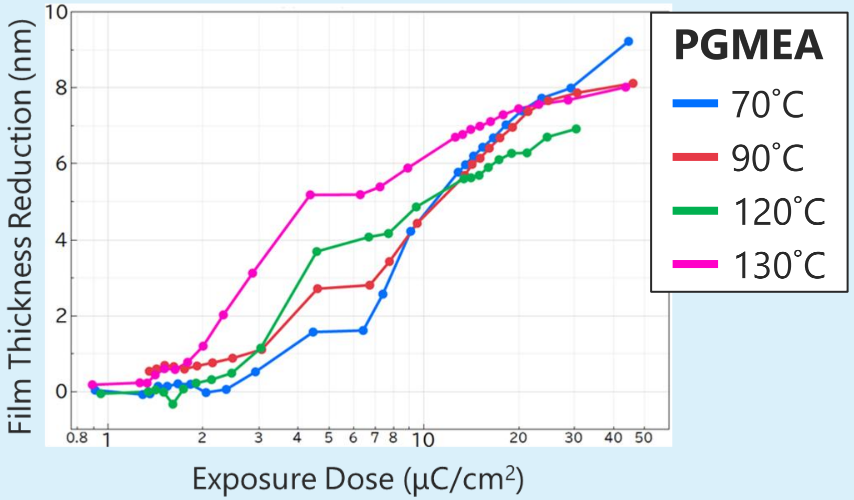
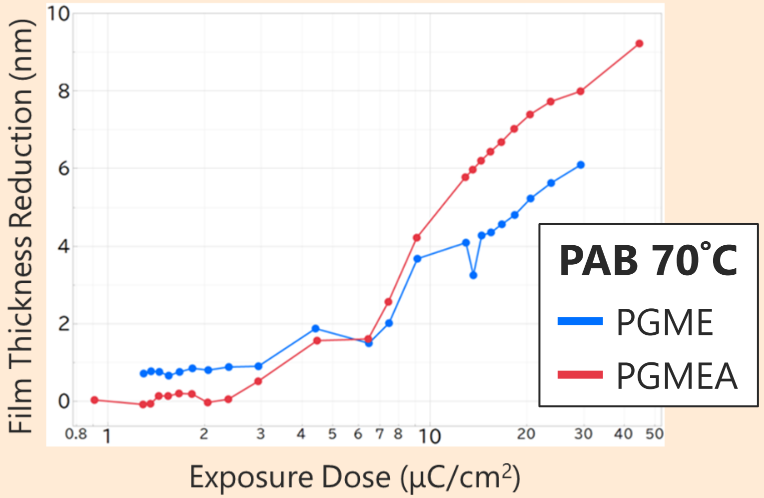
- ✓ For the sensitivity curves, the vertical axis shows film-thickness loss, T0 – T (nm).
- ✓ Horizontal shifts indicate sensitivity differences, while differences in vertical loss suggest differences in electron penetration behavior.

Effect of residual solvent





Effect of solvent species



As observed for EUV exposure, the response increased with PAB temperature and depended on solvent species.

→ This suggests that, at the same dose, the effective electron penetration or reaction depth differs among the samples.

Outline

Summary

✓ Residual solvent content depended on PAB temperature and solvent species.

✓ RSoXS indicated changes in chemical composition distribution or aggregation state in the resist thin film.

✓ XRR showed that sensitivity differences cannot be explained by average film density alone.

✓ EUV and LEEFET measurements showed higher sensitivity at higher PAB temperatures and for PGMEA-based samples.

✓ Trace residual solvent can affect the film environment and exposure response, suggesting that solvent and PAB optimization may help reduce LWR.

Thank you for your attention.

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